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Effects of Palladium Modification on Hydrogen Sorption by Boron Nitride with High Specific Surface Area

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1 Introduction

Since Dillon et al [1] reported plausibly high hydrogen capacity of single walled carbon nanotubes at room temperature; numerous researches have been made in order to develop highly efficient hydrogen storage media with high specific surface areas [2]. The maximum hydrogen capacity of single walled carbon nanotubes prepared by the authors was 0.86 mass% at room temperature under 0.1 MPa of hydrogen [3]. Those nanotubes contained Y and Ni, since the starting material was graphite compounded with those metals, which would act as catalysts to form tubular structures. Modification of high surface area materials with metals would be promising for construction of novel hydrogen storage composites, since some cooperative effect was found, for example, in a system comprising activated graphite and Zr [4]. BN can be prepared in a turbostratic layered form with high specific surface area [5], and there are more degrees of freedom to modify the structure as compared with carbonaceous compounds. In the present work, BN and Pd-modified BN samples with high specific surface areas were thus prepared by varied methods and their hydrogen storage capacities were evaluated.

2 Experimental

Preparation of BN was carried out by heating melamine borate, which was synthesized by mixing melamine and boric acid in hot water, first at up to 720 K in air for 110 min and secondly at 1170 K under nitrogen for 60 min. Modification of BN was carried out by three different methods. Non-electrolytic deposition (A) was performed using an aqueous solution of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$, EDTA and ammonia reduced by hydrazine. Modified BN was filtered, rinsed and dried overnight at 340 K. Immersion (B) was performed by sonicating BN in a methanol solution of palladium acetate. After filtration, rinsing and overnight drying at 340 K, the sample was heat treated at 520 K. Premixing followed by BN formation (C) was performed by sonicating melamine borate in an acetone solution of palladium acetate, filtration, rinsing, overnight drying at 340 K and heating at 1170 K under nitrogen.

The samples were characterized by SEM, XRD, FTIR and nitrogen adsorption measurements at 77 K. Hydrogen storage capacities were volumetrically evaluated at 297 K and 77 K.

3 Results and Discussion

Specific surface area of BN increased with that of starting melamine borate as shown in Figure 1. Since specific surface area of melamine borate was controllable by adjusting concentrations of melamine and boric acid, specific surface area of the calcined product, BN,

was also controllable in a range of 200-900 $\text{m}^2 \text{g}^{-1}$. The shape of BN observed by SEM was similar to that of melamine borate. The high specific surface area of BN would not be due to finely divided nature, but due to some porous structure of the sample.

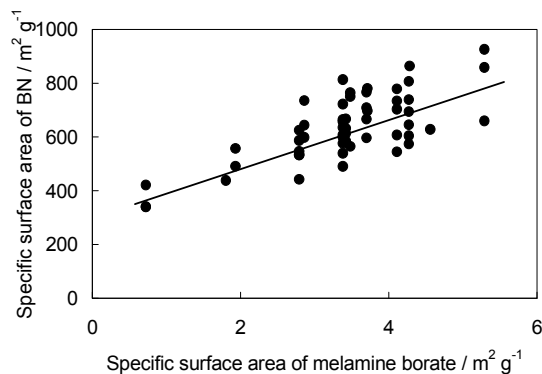


Figure 1: Variation of specific surface area of BN with that of melamine borate.

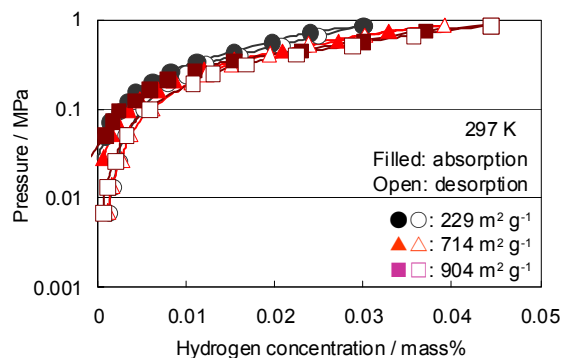


Figure 2: Hydrogen sorption isotherms at 297 K for BN with varied specific surface areas.

Hydrogen absorption-desorption isotherms in Figure 2 shows that the hydrogen storage capacity at room temperature was limited. Sorption was almost reversible and the amount of sorbed hydrogen rapidly increased under higher pressures. Sorption would proceed through physisorption. The hydrogen capacity increased with specific surface area as expected. Hydrogen sorption at 77 K was substantial as shown in Figure 3, and the amount of sorbed hydrogen again increased with specific surface area. Since the enhancement of sorption by cooling from room temperature to 77 K was about 50 times, the main scheme of sorption at 77 K would not be simple physisorption, but would be pore filling.

When modification of BN with Pd was carried out by the method (A) or (B) after the preparation of BN, the turbostratic structure of BN was completely or partly destroyed as illustrated in Figure 4, and specific surface areas of the Pd-modified samples were diminished from $514 \text{ m}^2 \text{g}^{-1}$ to $0.5 \text{ m}^2 \text{g}^{-1}$ for the method (A) and to $9 \text{ m}^2 \text{g}^{-1}$ for the method (B). In the case of the method (B), reflections from Pd were clearly observed in Figure 4. The intended dispersion of Pd was one Pd atom per nm^2 of the surface of BN, and the amounts of employed Pd compounds were weighed and added in accordance with that intension. Lowering of specific surface area of BN would cause excessive presence of Pd on the surface, and nucleation and growth of Pd particles would proceed to give the XRD pattern. On the other hand, the method (C), calcination of melamine borate preliminarily compounded with the palladium species, gave modified BN with large specific surface area as high as $800 \text{ m}^2 \text{g}^{-1}$, and the specific surface area value was adjusted by changing the nature of the starting melamine borate. The turbostratic layered structure of BN was clearly observed in the Pd-modified samples as shown in Figure 4.

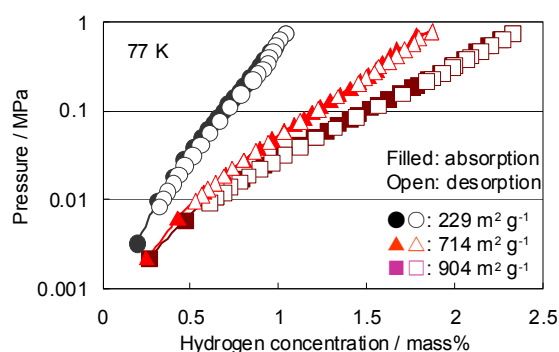


Figure 3: Hydrogen sorption isotherms at 77 K for BN with varied specific surface areas.

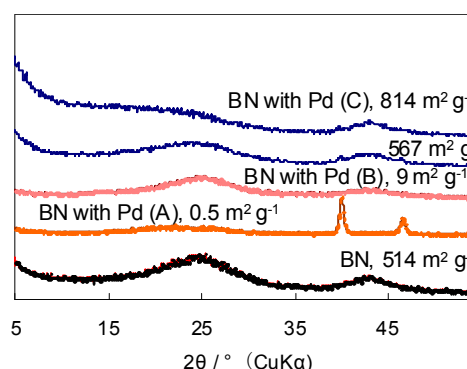


Figure 4: XRD patterns from BN and Pd-modified samples through different methods.

The method (C) gave porous structures to the modified samples, as was the case for BN itself, in addition to the layered structure. The presence of both micropores and mesopores was confirmed by the nitrogen adsorption isotherms in Figure 5 for the modified sample with specific surface area of $814 \text{ m}^2 \text{ g}^{-1}$. Its feature was similar to a typical neat BN with close specific surface area of $714 \text{ m}^2 \text{ g}^{-1}$ as illustrated in Figure 5. While the difference of micropore volume between BN and the modified BN was reasonable considering the difference of specific surface area, the difference of mesopore volume between them was not. In other words, reduction of mesopore volume was observed for the modified BN through the presence of Pd.

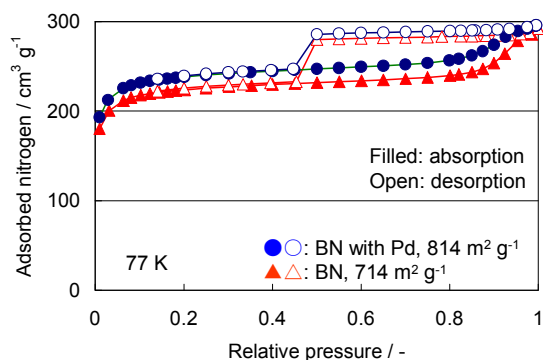


Figure 5: Nitrogen adsorption isotherms at 77 K for BN and a typical Pd-modified sample.

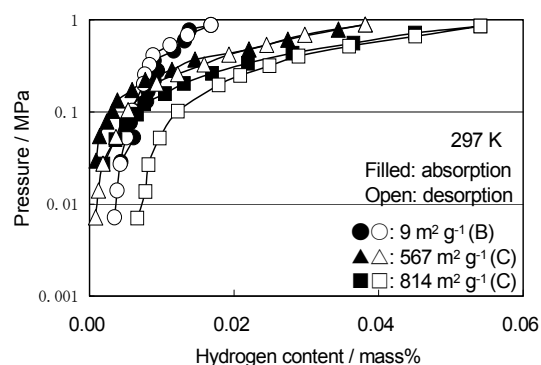


Figure 6: Hydrogen sorption isotherms at 297 K for Pd-modified BN samples with varied specific surface areas.

The modified BN with low specific surface area in Figure 6 sorbed less hydrogen than any BN in Figure 2. Collapse of the layered structure would be one of the causes of the reduction of the hydrogen capacity. The modified BN samples with high specific surface areas sorbed reasonable amounts of hydrogen as illustrated by the Isotherms in Figure 6. After the modification with Pd, some hydrogen irreversibly sorbed by the samples, although that was

not significant for the modified BN with specific surface area of $567 \text{ m}^2 \text{ g}^{-1}$. Figure 7 comparatively shows actual isotherms for the modified BN with specific surface area of $814 \text{ m}^2 \text{ g}^{-1}$ and calculated isotherms based upon a linear combination of isotherms for Pd and BN with a little bit larger specific surface area of $904 \text{ m}^2 \text{ g}^{-1}$. Hydrogen capacity of the modified sample exceeded the sum of that of neat BN and that of Pd, and a cooperative effect was observed at room temperature. That would be due to hydrogen dissociation sites provided by palladium and hydrogen accepting sites provided by BN. The irreversible nature again illustrated in Figure 7 for the modified BN suggested that those sites were chemisorption sites.

The cooperative effect would be found only for those modified samples with higher specific surface areas as suggested by Figure 8. The Pd modification would create the chemisorption sites on the victim of specific surface area nevertheless using the method (C).

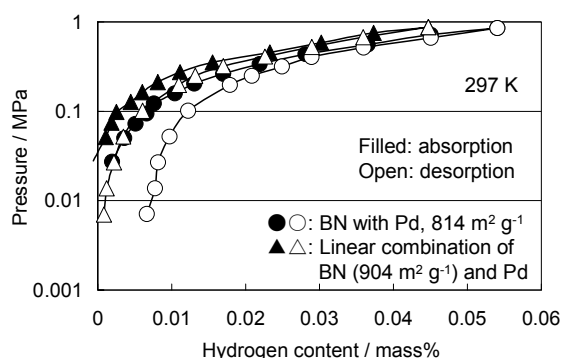


Figure 7: Comparative hydrogen sorption isotherms at 297 K for Pd-modified BN and a hypothetical mixture. The former is observed, and the latter is calculated on an assumption of simple mixing.

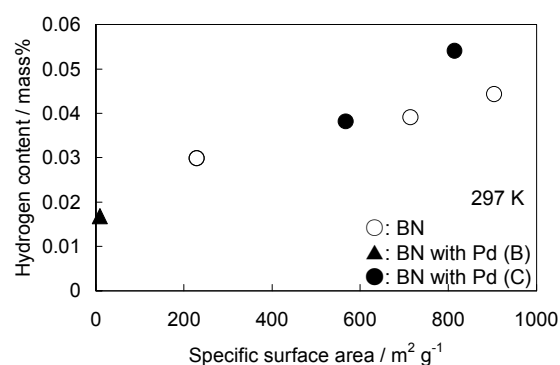


Figure 8: Variation of hydrogen sorption capacity at 297 K under 0.9 MPa with specific surface area for BN and Pd-modified samples.

The cooperative effect was not found at 77 K as shown in Figure 9. Isotherms for a modified sample with higher specific surface area almost coincided with those for BN with lower specific surface area. It is likely that pore filling of molecular hydrogen dominated at 77 K and that the presence of Pd would interfere with the filling flow of hydrogen. The reduction of the mesopore volume on the modification shown in Figure 5 supports that speculation. That is further depicted in Figure 10.

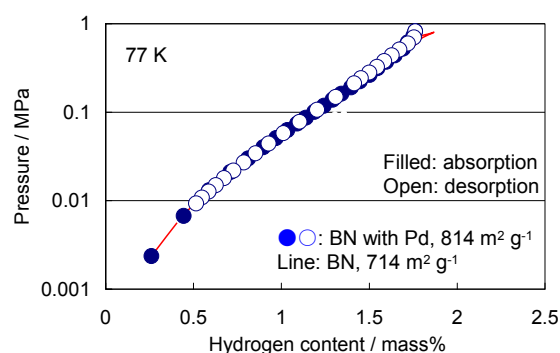


Figure 9: Comparative hydrogen sorption isotherms at 77 K for BN and a typical Pd-modified sample.

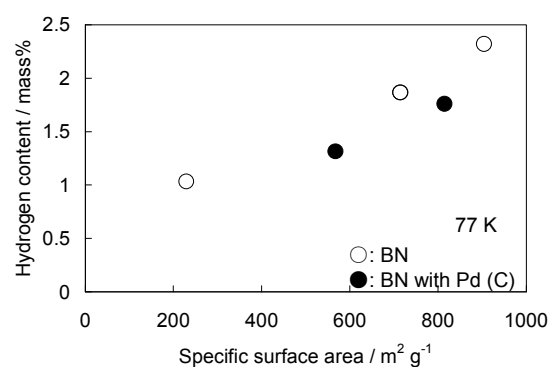


Figure 10: Variation of hydrogen sorption capacity at 77 K under 0.9 MPa with specific surface area for BN and Pd-modified samples.

4 Conclusion

BN modified with Pd had higher hydrogen capacity than the sum of hydrogen capacity of BN and that of Pd at room temperature, but such was not the case at 77K. Substantial hydrogen sorption of BN at 77 K would be due to micropores and mesopores, and that was not enhanced by the novel modification with Pd with high specific surface area retained. Specific surface area of BN increased with that of melamine borate, and hydrogen capacity increased with specific surface area of BN. That would be a guiding principle for constructing a new type of hydrogen storage material applicable at room temperature.

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